



A novel carbon thermal reduction approach to prepare recorded purity β -Ti₃O₅ compacts from titanium dioxide and phenolic resin



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ABSTRACT

β -phase titanium pentoxide (β -Ti₃O₅) has great potential applications in sensors, electrodes and laser devices, due to its unique phase-transforming behaviors. However, just this reversible phase transition behaviors between λ and β phases made its high purity preparation be challenging, and the high energy consumption of present industrialized method also limited the high-level applications of β -Ti₃O₅. In this work, a novel carbothermal reduction method has been acquired to produce highly pure β -Ti₃O₅ compacts from titanium dioxide “wrapped” by phenolic resin served as carbon source. Their phase and microstructure evolutions during the whole reaction process were systematically characterized under the assistance of Rietveld refinement and SEM images. The highly active pyrolytic carbon of phenolic resin could deposit on the surface of TiO₂ and this compacted state could promote the generated CO to accelerate the reaction process and decrease the addition of reductant, simultaneously. The reduction sequences were TiO₂ → Ti₄O₇ → Ti₃O₅ → Ti₂O₃. The weight ratio of phenolic to precursor of 9.0% could achieve the pure β -Ti₃O₅ as high as 98.06% under the calcination temperature of 1250 °C for 4 h. This work provided a novel and industrialized route to prepare β -Ti₃O₅ for applications in sensor and electrode in electrochemical reactions.

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1. Introduction

Recently, titanium pentoxide (Ti₃O₅), as an excellent phase-transformation material, has been widely used in the multifarious

potential applications such as data-storage, heat-storage, sensors, electrodes, ultrafast photoswitching, THz transmission medium and photocatalytic materials etc. [1–6]. More importantly, it has been used as an excellent high-index coating material to replace poor TiO₂ [7–9]. As known, the crystal structure of Ti₃O₅ is composed of distorted TiO₆ octahedron, which easily produces the different crystal phases (α , β , λ , γ and δ) induced by the real heat, light, atmosphere, temperature or pressure [10–13]. In addition, their electrochemical, thermoelectric, magnetic and optical properties during phase transformation processes have also been investigated to match the various application occasions [2,13–16].

Among all different crystal phases, β -phase exhibits the highest refractive index and it has been widely used in coating material [17]. Commercially, the redox reaction between metal powder of titanium (Ti) and titanium dioxide powder (TiO₂) is employed to

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prepare β -phase. The high temperature above 1800 °C for dozens of hours and the high vacuum (10^{-3} Pa) were required for the sufficient reduction. The serious problems of high energy consumption, high equipment requirements and high risk still existed in this commercial method. Therefore, the simple and efficient preparation approach for pure β -Ti₃O₅ was always pursued. However, almost no new approach was developed as far as we know.

In fact, a lot of titanium oxides are achieved by the thermal reduction reaction of TiO₂, and the synthesis of Ti₃O₅ should be no exception [18–20]. The reversible phase transition behaviors between λ phase and β phase always happened, and much attention has been focused on synthesizing nanoscale λ -Ti₃O₅. We think some signs or ideas should be found and inspired for the preparation of β phase from that of λ phase. Recently, the carbothermal reduction method was developed to synthesize nanocrystalline λ -Ti₃O₅ using carbon black as reduction agent, and the coated Al₂O₃ or doped MgO film as the second phase on the precursor TiO₂ nanoparticles effectively inhibited the grain growth and stabilized the phase at λ -Ti₃O₅ [21–23]. Therefore, the carbothermal reduction method made the low cost and high efficiency preparation of λ -Ti₃O₅ become possible [24–26]. Subsequent relevant studies based on these proposals were carried out to obtain λ -Ti₃O₅, although they are aimed at different application fields [27,28].

Obviously, the present method for λ -Ti₃O₅ could not be directly served for β phase due to the impurities addition, although it provided the excellent reference for the preparation of β phase [29]. As early as 2015, the addition of carbon black as high as 20 wt% at 1300 °C for 3 h in Ar atmosphere made the complete elimination of carbon impossible for the high purity of β phase. Although the β -Ti₃O₅ content was calculated to reach 90% by Rietveld refinement analysis, the Ti₂O₃ phase still existed as an impurity [2]. In fact, the high amount of carbon black was resulted from the point-point contact between TiO₂ and C. Therefore, seeking for a high efficient carbon source becomes an interesting and challenging issue.

As known, polyvinyl alcohol (PVA), was firstly proposed to mix with TiO₂ to synthesize Ti_nO_{2n-1} at 1100 °C, but β -Ti₃O₅ could not appear until the PVA content was over 40 wt% and Ti₄O₇ or Ti₂O₃ still coexisted in the products owing to the low effective carbon content [15]. Although this method failed to prepare high purity β -Ti₃O₅, the spark of “wrapping” of carbon source around TiO₂ really excited us to look for a high efficiency polymer resin to produce a large amount of high activity carbon residue under the high temperature to conduct the reduction process completely.

In this paper, a new approach for synthesizing high purity β -Ti₃O₅ was developed and the phenol resin was elutriated as the novel carbon source to wrap on the TiO₂ powders to enhance the reduction efficiency. The phase composition, morphology and reduction model (powders or compacts) were systematically investigated. The detailed reduction sequence of oxides was revealed to provide the deep insight on this novel approach under the assistance of XRD Rietveld refinement and other methods. Importantly, the commercial production route was provided by this paper, and its design idea and research train could promote the carbothermal reduction reaction for the low cost and high efficiency preparation of other similar oxides.

2. Experimental

2.1. Materials preparation

Titanium dioxide powder (TiO₂, 99.9%, X CJRNM, China), phenolic resin (C₇H₆O₂, 99.9%, Letian, China), and absolute ethyl alcohol (C₂H₆O, AR, Lingfeng, China) were used as raw materials to synthesize Ti₃O₅. The weight ratio of phenolic resin to the mixed powder was 8.0%, 8.5%, 9.0%, 9.5% and 10.0%, respectively. The TiO₂

powder was firstly dispersed in absolute ethyl alcohol solution with phenolic resin (weight ratio of mixed powder to absolute ethyl alcohol = 1:2), and then they were ball milled at 150 rad min⁻¹ for 24 h and the slurry was dried at 50 °C for 6 h in air. The dried precursor was ground together adequately in a mortar (~100 mesh) and pressed into compacts ($\Phi 22 \times 3$ mm) under uniaxial pressure of 10 MPa. At the same time, the compacts were annealed in the quartz-tube electric furnace (BTF-1700C, BEQ, China) with the gas flowing out for an hour before sintering process to remove contaminating gases that may be present. Subsequently, the compacts were annealed at 1100 °C–1300 °C for 2, 4 and 6 h under high-purity argon (99.999%) atmosphere with flow rate of 0.5 L min⁻¹ in a quartz-tube electric furnace and then cooled down to room temperature naturally. Finally, the obtained compacts were mechanically broken and ground into fine powders for further characterization.

2.2. Characterization methods

Phase evolution of the prepared materials was investigated by X-ray diffraction instrument (XRD, D2, Bruker, Germany) using Cu K α radiation in the range of 10°–80° (2 θ) with a step of 0.1° s⁻¹. The phase components of special samples were examined by XRD with a step of 0.01° and a counting time 1 s per step for Rietveld refinement analysis using the General Structure Analysis System (GSAS) software [30]. The morphology of the prepared materials was studied by scanning electron microscopy (SEM, JSM-6510, JEOL, Japan), and the decomposition behavior of phenolic resin was characterized by TG-DSC (SDT Q600, TA, America).

3. Results and discussion

Fig. 1(a) shows the decomposition process and carbon residue content of phenolic resin. The DSC curve exhibited a small exothermic peak arouse at 160 °C, which was considered as water evaporation, and the exothermic phenomenon near 825 °C indicated that the phenolic resin had sharply decomposed into carbon residue during heating process. Finally, the phenolic resin had completely decomposed at 955 °C and the carbon residue content was about 52.5 wt% form TG curve. As well known, the theoretical weight percentage of phenolic resin for preparing Ti₃O₅ in this carbon thermal reduction process was 9.1 wt% according to Eq. (1) [31]:



The XRD pattern of compact made from precursor powders with 9.0 wt% weight ratio of phenolic resin (red) and the rutile TiO₂ powder (black) are shown in Fig. 1(b). The characteristic diffraction peaks of precursor with phenolic resin seemed to be consistent with that of TiO₂. The morphology and Ti element mapping of a compact made by the ground powder indicating that TiO₂ powder was evenly distributed in the precursor (Fig. 1(c)–(d)).

Fig. 2 displays the phase compositions of the products made from precursors with phenolic resin weight ratio of 8.0%, 8.5%, 9.0%, 9.5%, 10.0% calcined at 1250 °C for 4 h. The characteristic diffraction peaks of Ti₄O₇ (PDF 71–1428), β -Ti₃O₅ (PDF 82–1138), and λ -Ti₃O₅ (PDF 82–1137) were simultaneously found in the reduced products made with weight ratio 8.0%, and it revealed that Ti₃O₅ could be reduced form TiO₂ at 1250 °C and the weight ratio of phenolic resin was too low to obtain pure Ti₃O₅. When the weight ratio increased to 9.0% and 9.5%, the compositions of the reduced products only consisted of β -Ti₃O₅ and λ -Ti₃O₅. Above 9.5 wt%, some Ti₂O₃ phase was found and this indicated the excessive phenolic resin caused the over-reduction of TiO₂. In consideration of the results shown in

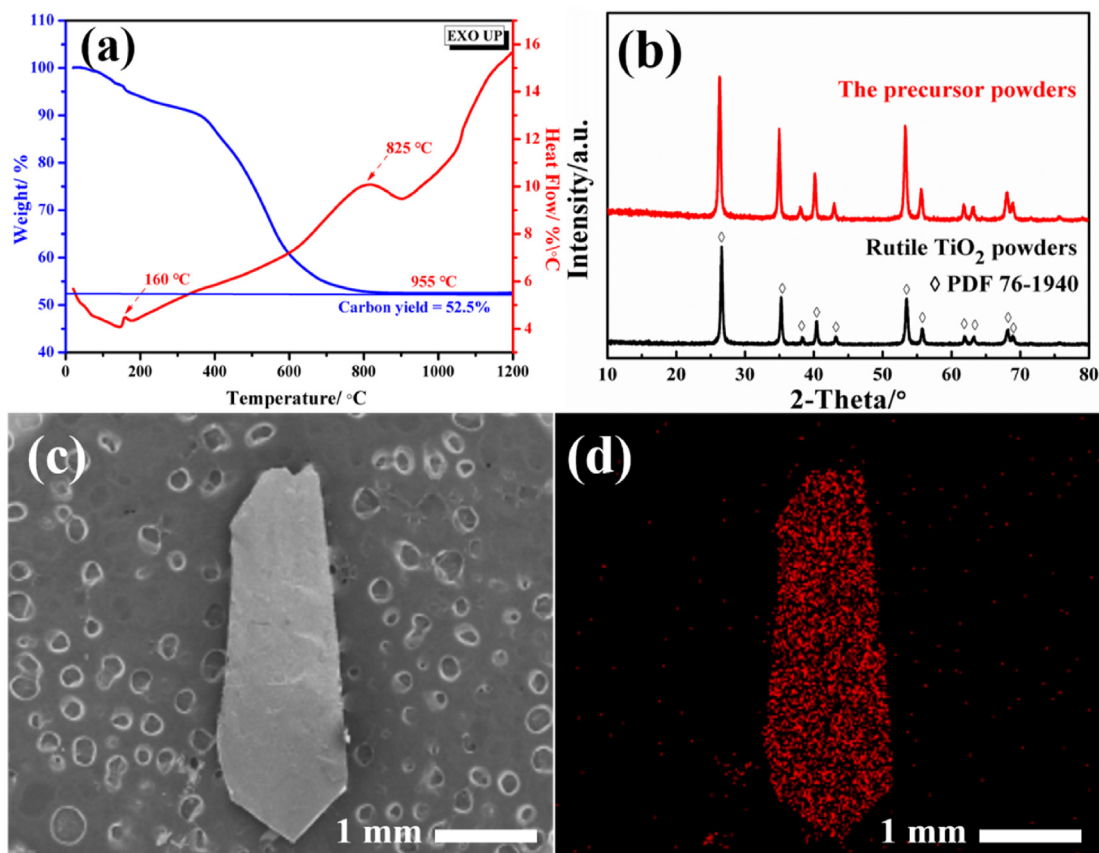


Fig. 1. (a) TG-DSC curve of the phenolic resin from room temperature to 1200 °C at heating rate of 20 °C min⁻¹ in argon atmosphere; (b) The XRD pattern of compact made from precursor powders with 9.0 wt% weight ratio of phenolic resin; (c) The SEM image of compacts made from powder with weight ratio of precursor compact; (d) Ti element mapping of precursor corresponding to (c).

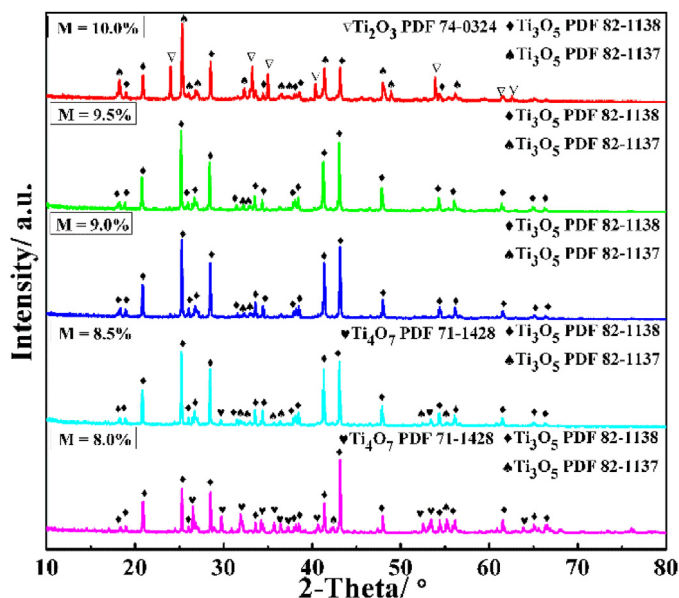


Fig. 2. The phases evolution of products synthesized with different weight ratio at 1250 °C for 4 h (M was the weight ratio of phenolic resin).

Fig. 1(a) and the calculated value from Eq. (1), the suitable and theoretical weight ratio of phenolic resin for synthesizing pure β - Ti_3O_5 was supposed at about 9.0 wt%.

Beside this, the phenolic resin weight ratio of 9.0% precursor was slightly lower than theoretical calculation value of 9.1 wt%. Because the following reactions as Eqs. (2)–(4) might occur during the reduction processes [32,33]:



In fact, TiO_2 powder could also be reduced by CO with the formation of CO_2 , which finally converted to CO by the Boudouard reaction in inert atmosphere [34]. The solid-state boundary reaction between TiO_2 and pyrolytic carbon from phenolic resin should be the main process while the reaction through gaseous intermediates (Eq. (3) and Eq. (4)) would proceed the whole reaction at the beginning of the reaction. As the reduction progressing, the reactions gaseous intermediates originated from (Eq. (2) and Eq. (4)) subsequently accelerated the rate of the whole reaction and decreased the amount of the reductant.

To confirm the compositions of the reduced products in the case of 9.0 wt% phenolic resin with different states from 1100 °C to 1300 °C for 4 h, the XRD patterns of products prepared from the precursor by 9.0 wt% phenolic resin at the various temperatures are presented in Fig. 3. For the compacted state of mixture, the product annealed at 1100 °C contained Ti_4O_7 phase with little uncertain diffraction peaks, but the Ti_3O_5 phase did not appear at this temperature in Fig. 3(a). With the temperature increasing to 1150 °C,

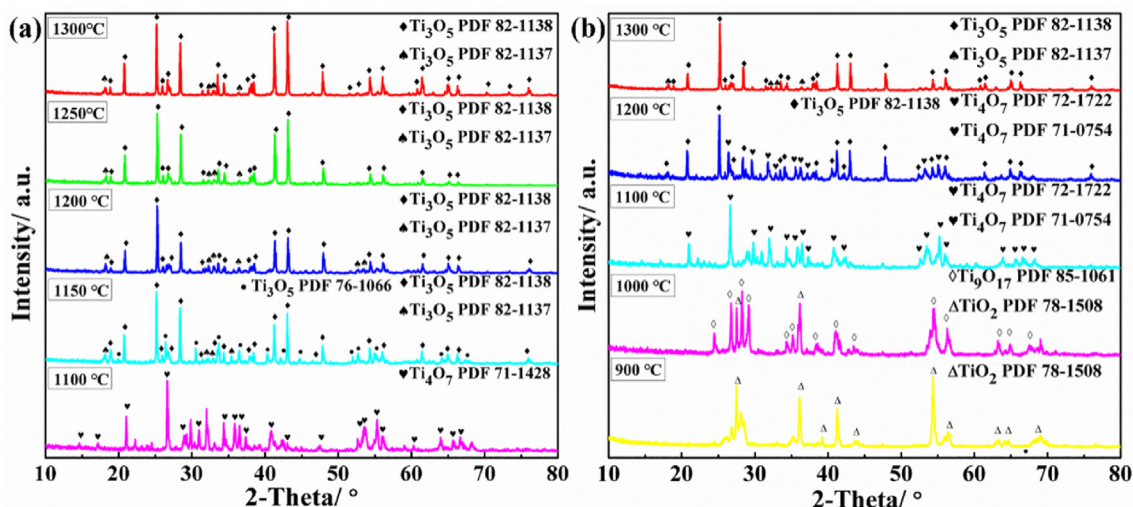


Fig. 3. The phases evolution of products prepared from the precursor by 9.0 wt% phenolic resin at various temperatures for 4 h at different states (a, compacted state; b, powder state).

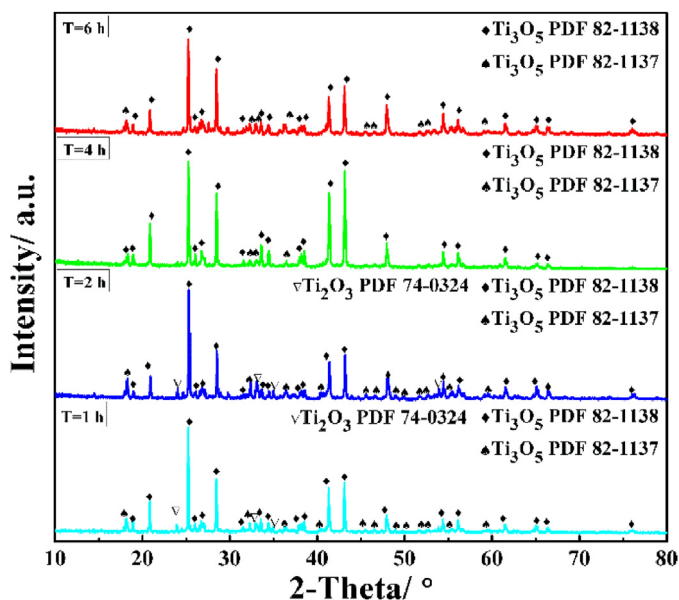


Fig. 4. Phase compositions of products prepared from the precursor by 9.0 wt% phenolic resin at 1250 °C for different times (T represented the holding time).

the three phases of Ti₃O₅ (α PDF 76–1066, β , λ) were detected with the disappearing of Ti₄O₇ phase due to the further reduction process. The characteristic diffraction peak intensity of β - and λ -Ti₃O₅ continued to increase with vanishing of α -Ti₃O₅ above 1200 °C [35]. The highly pure β -Ti₃O₅ phase with little λ -Ti₃O₅ was formed when the calcination temperature increased to 1250 °C indicating that this temperature was suitable for synthesizing high quality β -Ti₃O₅. However, for the powder state, it could be found from Fig. 3(b) that the suitable synthesis temperature of pure β -Ti₃O₅ was 1300 °C. The synthesis temperature of Ti₃O₅ compacted product was 50 °C lower than uncompact (powder) product. Therefore, the results indicated that the state of precursors was also very important to decrease the reaction temperature in same conditions. The reasons are proposed: firstly, the compacts can enlarge the contact area between pyrolytic carbon of phenolic resin and titanium dioxide, thus accelerating the surface reduction of titanium

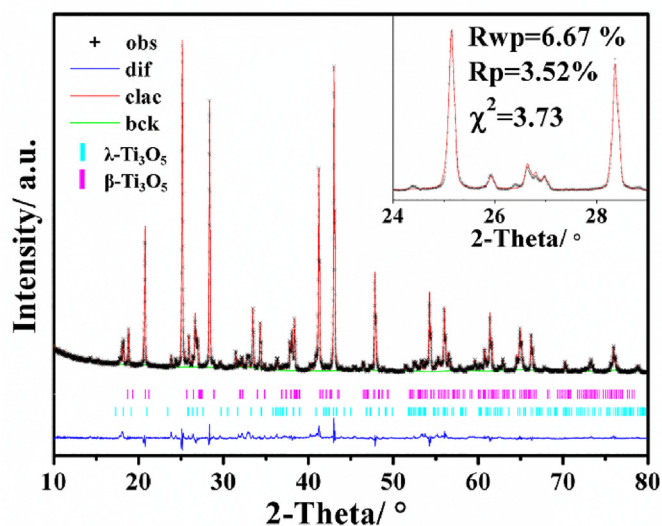


Fig. 5. Rietveld refinements (line) of the observed XRD patterns (+) for β -Ti₃O₅ synthesized at 1250 °C for 4 h with the phenolic resin concentration of 9.0 wt%. Vertical bars below the patterns show the position of all possible reflection peaks of their phases (Pink bars represented β -Ti₃O₅ phase, Blue bars represented λ -Ti₃O₅, and the inset exhibited the good fitting of strongest diffraction peak with the model). The lowest curve is the difference between the observed and the calculated intensities. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

dioxide with the generate CO. Secondly, the compact accumulation of powders in the compacts is conducive to limit the escaping of CO gas with the argon flowing out the open furnace, so CO plays the more important role in the reduction reaction than that in the uncompact state. In that case, the main reaction processes were likely to contain gas-solid and solid-state reaction between pyrolytic carbon and TiO₂ powder. These are the main reasons why the actual phenolic resin weight ratio of synthesizing Ti₃O₅ slightly is lower than the theoretical value.

In addition, the suitable holding time is significant for the solid-state and gas-solid reaction. To reveal the effect of holding time, the phase evolutions of the products made from the precursor with 9.0 wt% phenolic resin at 1250 °C for various times are given in

Table 1

The weight fractions of β -Ti₃O₅ in the products annealed at different temperatures for 4 h assisted by Rietveld refinement.

Phase composition	Annealing at 1200 °C	Annealing at 1250 °C	Annealing at 1300 °C
β -Ti ₃ O ₅	76.80%	98.06%	87.15%
λ -Ti ₃ O ₅	23.20%	1.94%	12.85%

Table 2

The lattice parameters of β -Ti₃O₅ are compared with those of previous literatures.

Parameters	a (Å)	b (Å)	c (Å)	Space group
This work	9.757	3.801	9.439	C2/m
Ref. [10]	9.752	3.802	9.442	C2/m
Ref. [2]	9.752	3.802	9.442	C2/m
Ref. [11]	9.748	3.801	9.441	C2/m

Table 3

The parameters of prepared Ti₃O₅ samples in previous literatures and those of this work.

Index File	Reductant	Content	Product	Purity	Addition
This work	Phenolic resin	9.0 wt%	β -Ti ₃ O ₅	98.06%	--
Ref [23]	Carbon black	4.50 wt%	λ -Ti ₃ O ₅	--	SiO ₂ , Al ₂ O ₃
Ref [27]	Carbon black	--	λ -Ti ₃ O ₅	--	SiO ₂ , TiO ₂
Ref [28]	Carbon black	3.80 wt%	β -Ti ₃ O ₅ , Ti ₄ O ₇	--	--
Ref [2]	Carbon black	4.49 wt%	β -Ti ₃ O ₅	90.5%	--

Fig. 4. The phase detected in the product made for 1 h were composed of Ti₃O₅ (β , λ) and Ti₂O₃ (PDF 74–0324), and the diffraction intensity of Ti₂O₃ increased when the holding time extended to 2 h. However, they faded away with holding time continued to prolong, which revealed that the suitable holding time of 4 h played a crucial role for preparing high quality β -Ti₃O₅. In addition, Ti₂O₃ as a component of overreduction product always appears in the reduction of Ti₃O₅. However, as an unstable titanium oxide during the carbon thermal reduction in argon atmosphere, Ti₂O₃ is also the intermediate that always appears before Ti₃O₅ appearance. The conclusion obtained in this work is similar with the previous experimental results reported by L. M. BERGER and Shinhoo Kang et al. [36]. The reason seems that the difference in the free energies of generation between Ti₂O₃ and Ti (C, O) with high

oxygen content is smaller than the difference between Ti₂O₃ and Ti₃O₅. The phase boundary between Ti₂O₃ and Ti₃O₅ can also be determined by considering the oxidation from Ti₂O₃ to Ti₃O₅.

In addition, the weight fraction of β phase in all samples was quantified using Rietveld method. The starting models for the refinements were taken from β -Ti₃O₅ and λ -Ti₃O₅ with space groups of C2/m and C2/m (difference in the ratio of lattice parameter, a/b/c), respectively. The profile was fitted using Pseudo-Voigt function. The typical Rietveld refinement plot (10°–80°) for Ti₃O₅ compact synthesized under the optimized conditions with the phenolic resin weight ratio of 9.0% is shown in Fig. 5. The R-values of this refinement were 6.67 (Rwp%), 3.52 (Rp%) and $\chi^2 = 3.73$, which suggested that the refinement was in good agreement with the space group in all respects. The weight fractions of the two phases were 98.06% (β) and 1.94% (λ), respectively. The Rietveld refinement results of the phase compositions of products calcined at different temperatures for 4 h are shown in Table 1. The lattice parameters of β -Ti₃O₅ compact and the previous reported are shown in Table 2. The lattice parameters of the samples were almost the same at different holding times. Obviously, the calcination temperature 1250 °C and holding time 4 h were the most suitable conditions for synthesizing the highest purity of β -Ti₃O₅ at 98.06%, and the higher or lower calcination temperature could lead to the different degree of degeneration of phase purity. In fact, as shown in Table 3, this is the recorded weight fraction of β phase due to the reversible phase transition behavior between λ phase and β phase under the preparation conditions without any impurities. For example, Al, Mg, Ce or W ions as the second phase was often used to stabilize the phase at λ or β -Ti₃O₅ depending on its amount [21,22,37]. Therefore, the preparation method and parameters in this work provided the highest purity of β -Ti₃O₅ required by the potential applications.

The SEM images of products synthesized at various calcination temperatures for 4 h with phenolic resin weight ratio of 9.0% are exhibited in Fig. 6. Evidently, it should be noted that Ti₃O₅ compact formed a porous structure in this compact and the single particle size was gradually increased from 1.0 μ m (1100 °C) to 2.0 μ m (1300 °C). As we know, this uniform and narrow distribution of Ti₃O₅ after grinding could be directly served for the coating-film applications. In addition, from Fig. 6(e), the pore size in the compact calcined at 1250 °C was in the range of 0.5–1.0 μ m. These porous compacts could be applied to electrochemical electrode materials, gas sensor materials and photocatalytic materials [15,27,38–40]. Therefore, in this work, the recorded purity of β -

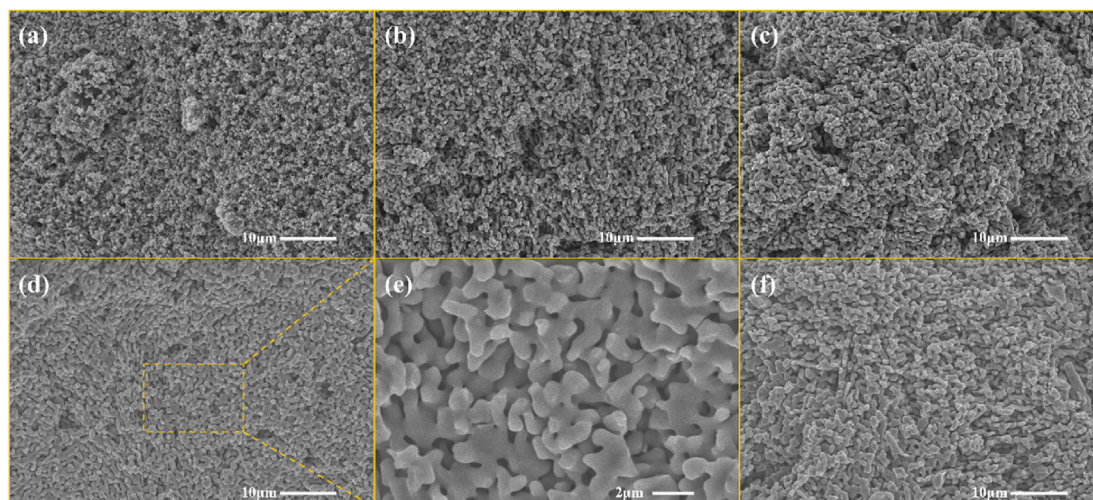


Fig. 6. SEM images of the products synthesized at various temperatures for 4 h: (a) 1100 °C, (b) 1150 °C, (c) 1200 °C, (d) 1250 °C, (e) the partial enlarge figure of (d), (f) 1300 °C.

Ti₃O₅ compact or powders could be obtained by this novel phenolic resin based on carbon thermal reduction, and this low cost and high efficiency route was also expected to apply in other similar oxides.

4. Conclusions

In this paper, the recorded purity β-Ti₃O₅ compacts were prepared through the novel phenolic resin based on carbon thermal reduction at 1250 °C for 4 h in Ar atmosphere, and the content of β phase in product was as high as 98.06%. The phenolic resin as an excellent carbon resource could wrap on the surface of TiO₂ powders to enhance the reduction efficiency, resulting in the simultaneously working of the solid-state and gas-solid reaction in the whole reduction process. Additionally, the compacted structure limited the escaping of CO gas during reaction process, hence the mainly reaction processes contained gas-solid and solid-state reaction between pyrolytic carbon and TiO₂ powders. Ti₄O₇ and Ti₂O₃ were produced as the intermediate products during the carbothermal reduction and the sequences of reduction was TiO₂ → Ti₄O₇ → Ti₃O₅ → Ti₂O₃. Finally, not only the proposed method in this study provided a commercial route to prepare industrial scale of Ti₃O₅ compacts, but also the designed idea and research train could also promote the carbothermal reduction reaction for the low cost and high efficiency preparation of other similar oxides.

CRedit authorship contribution statement

Shunshun Yang: Investigation, Methodology, Conceptualization, Experimental design, Formal analysis, Writing - original draft, Writing - review & editing. **Le Zhang:** Supervision, Methodology, Writing - review & editing, Funding acquisition, Validation, Resources. **Yuelong Ma:** Writing - review & editing. **Bingheng Sun:** Writing - review & editing. **Yinshuang Shan:** Writing - review & editing. **Zedi Shi:** Writing - review & editing. **Tianyuan Zhou:** Writing - review & editing. **Yun Wang:** Resources. **Farida A. Selim:** Resources. **Yanbin Li:** Resources. **Hongliang Li:** Resources, Funding acquisition. **Hao Chen:** Project administration, Supervision, Resources, Funding acquisition, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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